

POSTIRRADIATION EFFECTS: MONOMERS AND POLYMERS

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During August of 1955 while preparing some samples for an irradiation exhibit some postirradiation effects were observed. A 1:1 mixture of acrylonitrile and styrene and of methacrylic acid and styrene were placed in 6 by 12 in. 3-mil polyester film bags, the air bubbles removed, the bags heat sealed, and the contents irradiated to a slightly viscous consistency. The bags were then placed on a peg board in a room with northern exposure for a few weeks; following this exposure it was observed that the mixture had changed from a slightly viscous consistency to a firm, solid mass. Inasmuch as the diffusion of the monomer through the plastic film had been previously determined to be very low, it was inferred that postirradiation effects had completed the polymerization.

Although it was known at the time that many organic reactions, once initiated, proceed to completion under proper experimental conditions, no specific example had been scanned from the literature in which irradiation-induced polymerization of a slightly viscous liquid had been reported to proceed to completion as a consequence of postirradiation effects. Crazing in some polymeric materials, however, had been interpreted as a post-polymerization effect. A limited series of studies on postirradiation effects were initiated, accordingly, and some of the results of these "spot" experiments are reported in this paper.

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POSTHEATING OF IRRADIATED MONOMERS

Five-milliliter portions of various monomers were placed in 2 by 5 in. heat-sealed polyester film bags by use of a hypodermic syringe, the air bubbles removed, the bags resealed and strip packaged in polyethylene for convenience in handling, and then irradiated (with postheating after each pass) to the desired consistency. The bags were then opened, the contents transferred to a tared weighing bottle, weighed, and excess monomer allowed to evaporate on a hot plate at about 50 C. The samples were then placed in a vacuum oven at about 85 C for 4 hr to assure removal of all but traces of the monomer, conditioned in the balance room, weighed, and the amount of polymerization calculated. In some cases there was evidence of graft polymerization on the polyester film used as the container, but inasmuch as the bags had not been weighed previously the increase in weight was not determined.

In an attempt to isolate the heating effect, seven samples, each of 5-ml. portions, of various monomers were placed in 5-in. constricted test tubes, the tubes chilled and sealed, and strip packaged in polyethylene. The samples were then given a single pass under an electron beam which was set to deliver 0.1 mega-rad per pass, then placed in an oven at 75 C and samples withdrawn for analysis after 0, $\frac{1}{2}$, 1, 2, 4, 6, and 24 hr. The tubes were then opened and the contents of each tube transferred to a tared weighing bottle, weighed, and the excess mono-

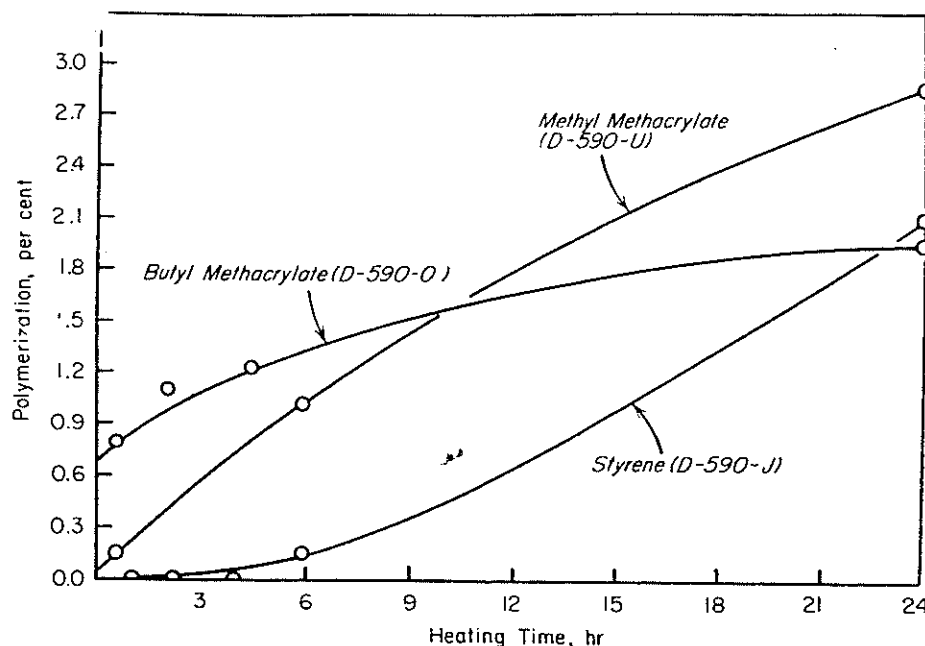


FIG. 1.—Percentage of Polymerization Versus Postirradiation Heating Time for Three Monomers. One pass each at 0.1 megarad.

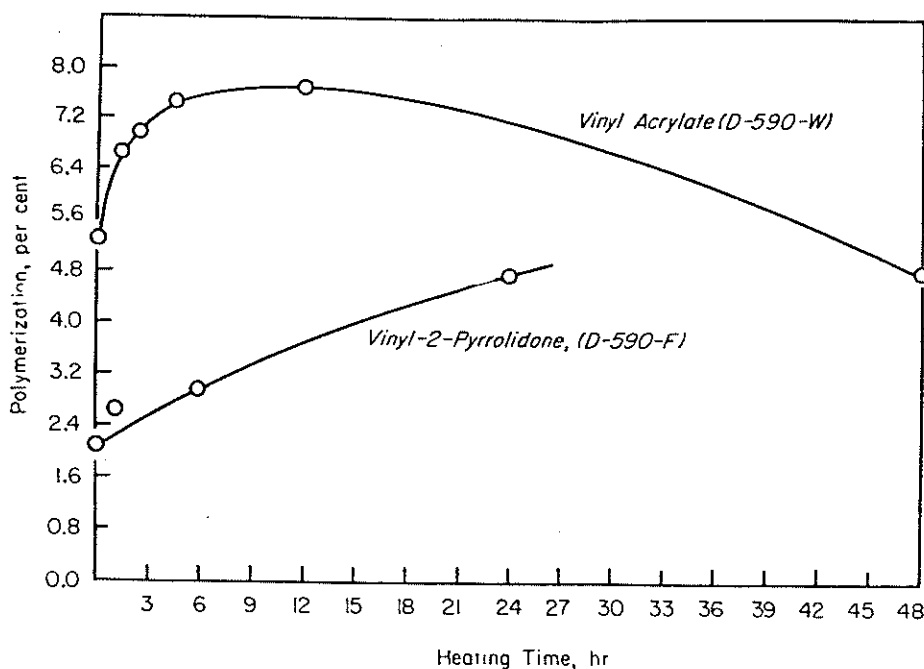


FIG. 2.—Percentage of Polymerization Versus Postirradiation Heating Time for Two Monomers. One pass each at 0.1 megarad.

mer allowed to evaporate on a hot plate at about 50 C. The weighing bottles were then placed in a vacuum oven at about 85 C to ensure removal of all but traces of the monomer, and the weights of the

residues were determined. The results for five of the monomers are shown graphically by Figs. 1 and 2, in which the percentage of polymerization is plotted against the postirradiation heating time.

TABLE I.—STYRENE MONOMER: POSTIRRADIATION EFFECTS AT DIFFERENT DOSE RATES, ATMOSPHERES, AND POSTIRRADIATION STORAGE CONDITIONS.^a

| Series | Rads per Pass | Total Dose, rads | Postirradiation Effects, per cent polymerized in | | | | | |
|--------------------|------------------|------------------|---|----------------------|-----------------------|--------------------------------|------------------------|------------------------|
| | | | Average, Sample D-643-6 | Sample D-642 in Air | Sample D-643 in Argon | Sample D-644 in Carbon Dioxide | Sample D-645 in Helium | Sample 646 in Nitrogen |
| 00— a b c | Control | 0 | 0.0 0.0 0.0 | 0.0 0.0 0.0 | 0.0 0.1 0.1 | 0.0 0.0 0.0 | 0.0 0.0 0.0 | 0.0 0.0 0.0 |
| 0— a b c | | | 5.5 5.5 10.0 | 9.6 9.6 16.0 | 5.5 5.6 10.1 | 5.5 5.6 10.0 | 5.4 5.5 10.0 | 5.6 5.4 9.7 |
| 1— a b c | 1×10^3 | 1×10^4 | 4.0 4.4 8.6 | 6.2 7.5 16.4 | 4.1 4.4 8.5 | 4.0 4.4 8.5 | 4.0 4.3 8.7 | 4.1 4.3 8.6 |
| 2— a b c | 5×10^3 | 5×10^4 | 4.2 4.4 8.5 | 6.4 7.7 14.4 | 4.2 4.5 8.5 | 4.6 4.4 8.6 | 4.1 4.3 8.6 | 4.1 4.4 8.3 |
| 3— a b c | 10×10^3 | 10×10^4 | 4.6 4.6 8.8 | 5.8 5.5 14.2 | 4.6 4.6 8.7 | 4.5 4.5 9.0 | 4.8 4.8 9.2 | 4.4 4.4 8.4 |
| 4— a b c | 25×10^3 | 25×10^4 | 5.3 5.7 10.0 | 6.2 7.7 20.3 | 5.6 5.9 9.9 | 5.4 5.7 10.1 | 5.2 5.6 10.0 | 5.2 5.6 10.0 |
| 5— a b c | 50×10^3 | 25×10^4 | 4.5 4.7 8.6 | 5.6 5.6 15.1 | 4.7 4.9 8.6 | 4.5 4.4 8.4 | 4.3 4.6 8.8 | 4.6 4.8 8.6 |
| 6— a b c | 10×10^4 | 50×10^4 | 5.6 5.7 10.3 | 5.8 5.7 13.3 | 6.2 6.0 10.5 | 5.8 5.5 10.2 | 4.9 5.7 10.2 | 5.4 5.6 10.1 |
| 7— a b c | 50×10^4 | 25×10^5 | 11.1 10.7 15.6 | 7.8 7.6 15.0 | 10.6 10.4 15.0 | 11.0 10.9 17.3 | 11.1 10.7 18.0 | 11.7 10.7 12.0 |
| 8— a b c | 10×10^5 | 50×10^5 | 22.5 ^b 24.6 ^b 26.9 ^b | 11.5 11.7 23.0 | 17.1 17.6 22.9 | 23.5 24.5 25.7 | 21.5 24.7 28.0 | 9.7 10.3 14.5 |
| 9— a b c | 15×10^5 | 75×10^5 | 27.0 ^b 30.7 ^b ... | 11.7 12.6 23.3 | 20.4 18.1 22.5 | 25.9 29.4 19.6 | 28.1 31.9 35.0 | 11.4 10.5 15.2 |

^a Samples in series 1 to 4 had ten passes each, with 1 hr postheating at 75 C after each pass, whereas samples in series 5 to 9 had only five passes and five postheatings. The "a" samples were processed promptly, the "b" samples were refrigerated for 5 days, and the "c" samples were postheated for 5 days at 50 C.

The 1 by 12 in. constricted test tubes were all flamed out under vacuum, the desired gas introduced and 20 ml of the freshly distilled styrene added. The tubes were then chilled in an alcohol-dry ice mixture, and evacuated and filled with the desired gas three times before sealing off and packaging for irradiation.

^b Carbon dioxide and helium average only.

It was incorrectly assumed that any postirradiation effects would be terminated in an hour or more, hence heat control samples were prepared for only the $\frac{1}{2}$ -, 1- and, 2-hr postheating periods. The 2-hr heat control sample for butyl methacrylate, for example, yielded only 0.1 per cent polymer as compared with 1.1 per cent for the corresponding irradiated sample, and the vinyl acrylate 2-hr heat control contained 0.2 per cent polymer whereas the corresponding irradiated sample yielded 5.2 per cent polymer. The relative contribution made by the irradiation and the postheating for the longer periods cannot be evaluated from the available data.

From Figs. 1 and 2 it is observed that the postirradiation heating effect appears to be a function of the type of monomer and that the optimum yield of polymer from vinyl acrylate was obtained after about 6 hr. For practical reasons these monomers were used as they came from the manufacturer without further purification. It is planned to repeat portions of these studies in glass test tubes under more carefully controlled conditions with respect to various factors such as atmosphere, dose rate, temperature, and others.

STYRENE: DOSE RATE, ATMOSPHERE, AND STORAGE

Freshly distilled styrene monomer (20 ml) was introduced into each of 165 constricted test tubes, 1 by 12 in. in size which were flamed out under vacuum and the desired atmosphere introduced before addition of the styrene. The tubes of styrene were then chilled for $1\frac{1}{2}$ min in an alcohol - dry ice mixture, evacuated to about 1 mm of mercury, and filled with the desired atmosphere. Two additional evacuations and fillings with the indicated atmosphere, together with the flaming out of the tubes initially, assured removal of all but traces of oxygen and moisture in the tubes containing argon,

carbon dioxide, helium, and nitrogen, other than amounts normally present in the monomer and in these commercial gases.

The plan of the experiment is indicated in Table I where the results are tabulated for the five atmospheres used and for the different dose rates and the different post-storage conditions. In this paper, dose refers to exposure or delivered dose and dose rate should be interpreted as "exposure-dose rate." Where 1 by 12-in. pyrex test tubes were used as the irradiation container, the absorbed dose was approximately 60 per cent of the exposure or delivered dose. The results for atmospheres of air and helium are shown graphically by Figs. 3 and 4. The high values for the heat controls might be attributed to an error in technique inasmuch as these tubes were left in the oven continuously, whereas all other tubes were removed every hour for an additional pass under the beam which resulted in some cooling even though the warm trays were insulated from the conveyor chain by about 1 in. of polystyrene foam.

The graphs of Figs. 3 and 4 are shown in two sections: the one to the left represents 10 passes at the indicated dose rate (Table I), and the one to the right only 5 passes.

There is no apparent significant difference between the results for the "a" samples which were processed promptly and those of the "b" samples which were refrigerated 5 days. This consistency of pattern serves as a check on the experimental procedure, inasmuch as little change should be expected during the refrigeration. The "c" samples, which were heated 5 days at 50 C, contained significantly more polymer (except sample 9-c) than did the corresponding "a" and "b" samples. The effect of air was most pronounced at the lower dose rates, whereas the helium atmosphere gave the highest yield of polymer at the highest dose rate.

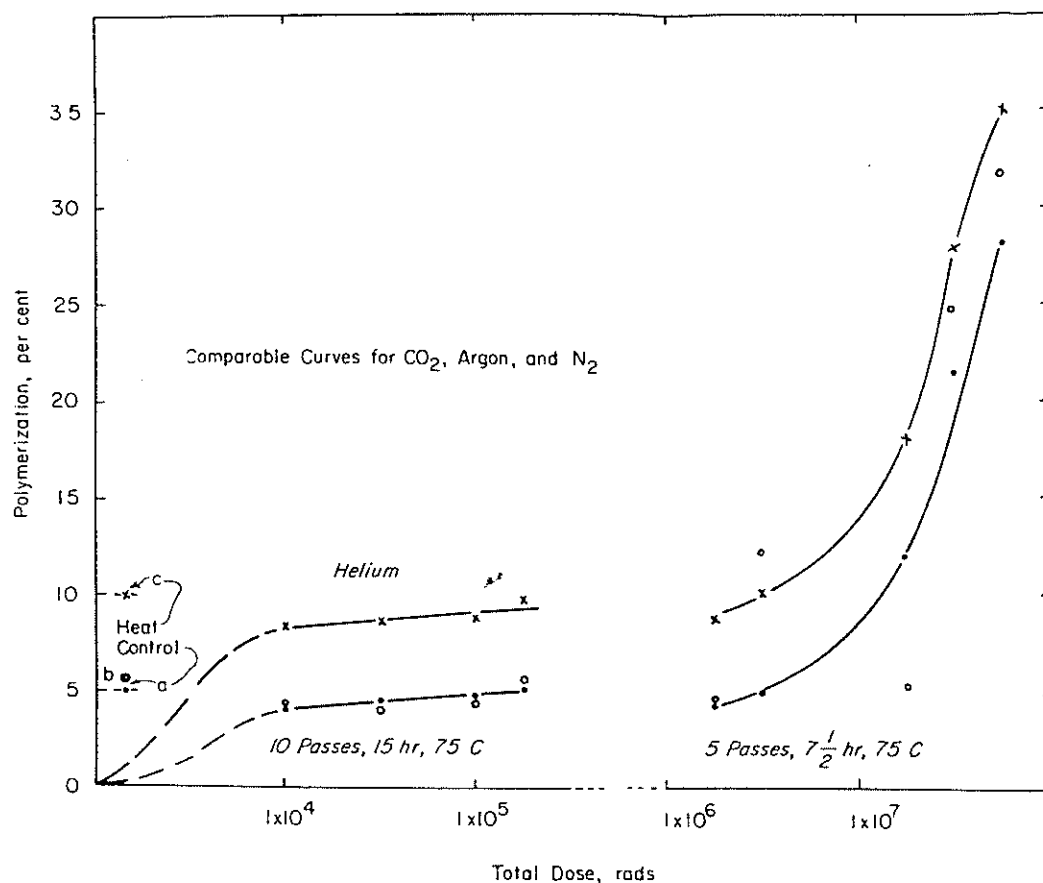


FIG. 3.—Irradiation of Styrene in Different Atmospheres and at Different Dose Rates. Postheating temperature 50 C. Lower curve, "a" and "b" values; upper curve, "c" values.

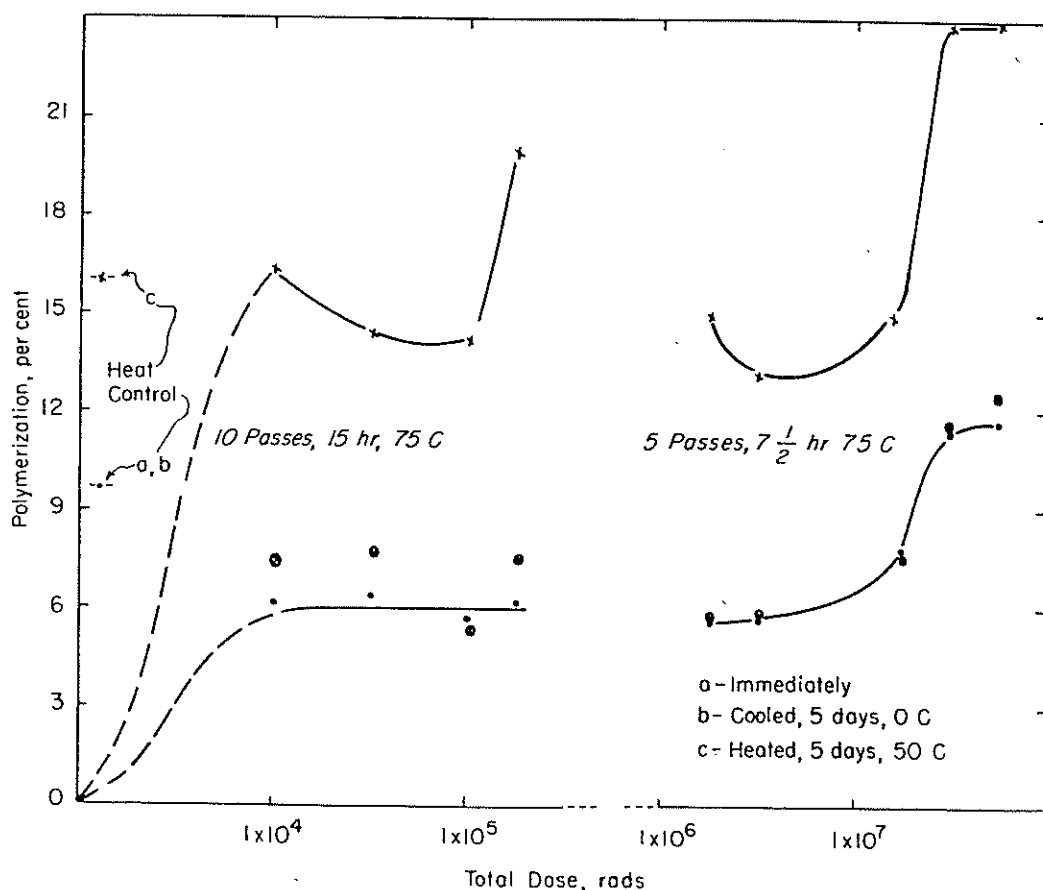


FIG. 4.—Styrene (Sample D-642): Postirradiation Effects in Air. Lower curve, "a" and "b" values; upper curve, "c" values.

TABLE II.—POSTHEATING VALUES MINUS HEAT CONTROL VALUES BY DOSE RATE AND ATMOSPHERE FROM TABLE I.

| Dose Rate, rads | Air | Argon | Carbon Dioxide | Helium | Nitrogen |
|------------------------|------|-------|----------------|--------|----------|
| Heat Control.. | 6.4 | 4.6 | 4.5 | 4.6 | 4.1 |
| 1×10^3 | 9.8 | 4.4 | 4.5 | 4.7 | 4.5 |
| 5×10^3 | 8.0 | 4.3 | 4.0 | 4.5 | 4.2 |
| 10×10^3 | 8.4 | 4.1 | 4.5 | 4.4 | 4.0 |
| 25×10^3 | 14.1 | 4.0 | 4.7 | 4.8 | 4.8 |
| 50×10^3 | 9.5 | 3.9 | 3.9 | 4.5 | 4.0 |
| 10×10^4 | 12.2 | 4.3 | 4.4 | 4.3 | 4.7 |
| 50×10^4 | 7.2 | 4.4 | 6.3 | 6.9 | 0.3? |
| 10×10^5 | 11.5 | 5.8 | 2.2 | 6.5 | 4.8 |
| 15×10^5 | 11.6 | 2.1 | -6.3? | 6.9 | 3.8? |

tion made by these two factors, dose rate and heating time.

If one considers the corresponding results for groups 1, 2, and 3, there is in general little or no change in the amount of polymer obtained, despite the fact that group 2 received five times as much irradiation as group 1 and that group 3 received twice as much irradiation as group 2. This indicates that the "efficiency" of irradiation-induced polymerization decreases with an increase of dose, as has been observed by other investigators at much lower dose rates and

TABLE III.—REPRODUCIBILITY OF RESULTS IN IRRADIATION-INDUCED POLYMERIZATION OF MONOMERS.

| Code | Monomer | Dose | Polymerization, per cent |
|--------------|----------------------------|-------------------------|--------------------------|
| D558A3a b | Styrene/high vacuum | 3 passes at 0.1 megarad | 7.33 |
| | | | 7.33 |
| D558A3c d | Styrene in benzene: 1 to 1 | 3 passes at 0.1 megarad | 3.88 |
| | | | 3.63 |
| D558B3a b | Styrene/normal vacuum | 3 passes at 0.1 megarad | 6.76 |
| | | | 7.09 |
| D558F2a b | Styrene/helium | 3 passes at 0.1 megarad | 3.01 |
| | | | 2.77 |

The results for argon, carbon dioxide, helium, and nitrogen appear reasonably comparable for the lower dose rates, but variation becomes quite apparent at the higher dose rates.

In Table I it is noted that samples 4-a, b, and c had the same total dose as did samples 5-a, b, and c, but that the dose rate for the former is only one half of that for the latter and that the total heating time of group 4 is 15 hr as compared to $7\frac{1}{2}$ hr for group 5. Comparison of the results for the samples in group 4 with those for the corresponding samples of group 5 clearly indicates that the lower dose rate and the additional heating time yield more polymer without exception. From the data available one cannot estimate the relative contribu-

tion in this and other systems in this laboratory.

All tubes in this series were irradiated on the same day. They received about $\frac{1}{2}$ hr of preheating at 75 C and 1 hr of postheating after each pass, plus a final postheating of 2 hr. The series of tubes in groups 1 to 4 received a comparable treatment two weeks later (refrigerated during the interim), or a total of 10 passes and 15 hr of heating at 75 C. Irradiation was done with a $1\frac{1}{2}$ -Mev Van de Graaff accelerator, operating at 2 Mev.

Referring again to Table I, if one subtracts the 0-a from the 0-c values for the respective atmospheres, the contribution of the postheating is isolated, which should remain constant for the different dose rates. If in turn one subtracts the

"a" values from the corresponding "c" values for the irradiated samples, the total effect for postirradiation and post-heating is obtained. These values are shown by dose rate and atmosphere in Table II.

Any deviation from the heat control values of the first line of Table II and the subsequent values should be assigned to a postirradiation effect. This deviation is most pronounced in the air atmosphere, but also becomes apparent in the other atmospheres at the higher dose rates. It is observed also from this table that certain dose rates and atmospheres contribute to a higher yield of polymer than that obtained by the next higher dose rate and a higher total dose in the same atmosphere. This apparent inconsistency has been observed elsewhere in our studies and must be attributed at present to different reaction mechanisms or different combinations of mechanisms as a function of dose rate, total dose, and atmosphere.

Table III is included to indicate further the reproducibility of results by this experimental procedure. In Table II, accordingly, it may be assumed that a deviation of 0.4 or less may be attributed to experimental error but that larger values appear to be significant.

To determine the percentage of polymer formed, the tubes were opened, the contents transferred to a tared aluminum foil dish, the tube rinsed three times with methyl ethyl ketone, the rinsings added to the dish, which should have obliterated any reactive centers, and the dishes placed on a hot plate at about 50 C for removal of diluent and most of the excess monomer. The dishes were then placed in a vacuum oven at 85 C for 4 hr to assure removal of all but traces of the monomer, and conditioned in the balance room and weighed to determine the amount of polymer residue. The percentage of polymerization was calculated from the 20 ml of styrene initially bu-

retted into the tubes and the weighed residues of polymer.

These results emphasize, among other things, the irradiation "factor-dependency" of styrene and suggest that other monomer systems might respond to very slight variations in irradiation procedure.

Closely related work includes that of: Martin of the University of Michigan, who reported that the "viscosity of monomeric styrene after irradiation in a cobalt-60 source continued to increase after the samples were withdrawn from the source, while unirradiated check samples remained unchanged;"² Fox and Alexander who observed that methacrylic acid precipitated from a concentrated solution during irradiation is capable of "initiating polymerization in methacrylic acid even after having been exposed to air for some time;"³ Majury, who found that methyl methacrylate, exposed to 1.5×10^5 reps, yielded 1 per cent polymer after 6 hr and 5 per cent after 50 hr;⁴ and Dole of Northwestern University who found that polyethylene, when packaged and irradiated so that changes in pressure could be observed, depleted the atmosphere as observed by a drop in pressure when stored in the dark for a period of hours. This was attributed to an uptake of oxygen by activated areas on the irradiated polyethylene.⁵

COTTON DUCK: DOSE RATE, ATMOSPHERE, STORAGE

In an attempt to determine the post-irradiation effects on cotton duck (12 oz), an experiment was designed (Table IV)

² J. J. Martin et al, "Utilization of the Gross Fission Products," Progress Report 3, University of Michigan (1952).

³ M. Fox and P. Alexander, "After-effects of the X-Ray Induced Polymerization Reactions of Methacrylic Acid in Aqueous Solutions" (in French), *Journal de chimie Physique*, Vol. 52, p. 710 (1955).

⁴ T. G. Majury, "Polymerization of Methyl Methacrylate by Pulses of High-Energy Electrons," *Journal of Polymer Science*, Vol. 15, p. 297 (1955).

⁵ Malcolm Dole, Private communication.

TABLE IV.—COTTON DUCK: POSTIRRADIATION EFFECTS AT DIFFERENT DOSE RATES, ATMOSPHERES, AND POSTIRRADIATION STORAGE CONDITIONS.^a

| Series | Rads per Pass | Sample D-637 in Air | | Sample D-638 in Argon | | Sample D-639 in Carbon Dioxide | | Sample D-640 in Helium | | Sample D-641 in Nitrogen | |
|----------------|------------------|---------------------|-----------------------------------|-----------------------|-----------------------------------|--------------------------------|-----------------------------------|------------------------|-----------------------------------|--------------------------|-----------------------------------|
| | | Weight Loss, avg, g | Tensile Strength, avg, lb per in. | Weight Loss, avg, g | Tensile Strength, avg, lb per in. | Weight Loss, avg, g | Tensile Strength, avg, lb per in. | Weight Loss, avg, g | Tensile Strength, avg, lb per in. | Weight Loss, avg, g | Tensile Strength, avg, lb per in. |
| 00—a b c | Control | -0.0497 | 163 | +0.0111 | 160 | -0.0622 | 158 | -0.0674 | 161 | -0.0612 | 162 |
| | | -0.0494 | 161 | -0.0492 | 168 | -0.0547 | 158 | -0.0561 | 161 | -0.0439 | 163 |
| | | -0.0478 | 159 | -0.0509 | 167 | -0.0509 | 160 | -0.0540 | 162 | -0.0283 | 164 |
| 0—a b c | Heat Control | -0.0619 | 161 | -0.0570 | 166 | -0.0640 | 154 | -0.0679 | 155 | -0.0539 | 165 |
| | | -0.0506 | 161 | -0.0529 | 160 | -0.0542 | 159 | -0.0603 | 160 | -0.0487 | 160 |
| | | -0.0510 | 151 | -0.0557 | 159 | -0.0530 | 164 | -0.0542 | 157 | -0.0459 | 161 |
| 1—a b c | 1×10^3 | -0.0614 | 165 | -0.0630 | 166 | -0.0594 | 160 | -0.0740 | 165 | -0.0609 | 167 |
| | | -0.0530 | 161 | -0.0395 | 165 | -0.0490 | 161 | -0.0649 | 159 | -0.0489 | 158 |
| | | -0.0557 | 149 | -0.0318 | 161 | -0.0496 | 158 | -0.0672 | 153 | -0.0468 | 160 |
| 2—a b c | 5×10^3 | -0.0654 | 164 | -0.0263 | 165 | -0.0622 | 158 | -0.0801 | 165 | -0.0625 | 166 |
| | | -0.0567 | 160 | -0.0490 | 159 | -0.0536 | 159 | -0.0722 | 155 | -0.0536 | 154 |
| | | -0.0573 | 150 | -0.0400 | 157 | -0.0532 | 150 | -0.0700 | 153 | -0.0521 | 160 |
| 3—a b c | 10×10^3 | -0.0683 | 159 | -0.0436 | 166 | -0.0690 | 160 | -0.0842 | 165 | -0.0545 | 162 |
| | | -0.0606 | 160 | -0.0559 | 163 | -0.0515 | 149 | -0.0750 | 151 | -0.0548 | 160 |
| | | -0.0637 | 156 | -0.0548 | 162 | -0.0604 | 163 | -0.0715 | 159 | -0.0552 | 161 |
| 4—a b c | 25×10^3 | -0.0716 | 164 | -0.0657 | 156 | -0.0717 | 151 | -0.0970 | 155 | -0.0635 | 156 |
| | | -0.0635 | 158 | -0.0582 | 161 | -0.0669 | 156 | -0.0737 | 155 | -0.0564 | 160 |
| | | -0.0675 | 149 | -0.0603 | 159 | -0.0629 | 154 | -0.0730 | 151 | -0.0335 | 158 |
| 5—a b c | 50×10^3 | -0.0727 | 151 | -0.0498 | 155 | -0.0719 | 150 | -0.0847 | 145 | -0.0676 | 153 |
| | | -0.0625 | 151 | -0.0433 | 151 | -0.0628 | 147 | -0.0697 | 152 | -0.0570 | 152 |
| | | -0.0543 | 139 | -0.0370 | 149 | -0.0562 | 154 | -0.0611 | 150 | -0.0473 | 152 |
| 6—a b c | 10×10^4 | -0.0663 | 145 | ... | 143 | -0.0562 | 143 | -0.0787 | 142 | -0.0637 | 146 |
| | | -0.0578 | 140 | -0.0459 | 148 | -0.0567 | 144 | -0.0664 | 135 | -0.0531 | 146 |
| | | -0.0618 | 133 | -0.0526 | 141 | -0.0553 | 145 | -0.0633 | 143 | -0.0523 | 145 |
| 7—a b c | 50×10^4 | -0.0865 | 99 | -0.0887 | 103 | -0.0898 | 101 | -0.0955 | 102 | -0.0822 | 97 |
| | | -0.0796 | 101 | -0.0823 | 102 | -0.0777 | 106 | -0.0829 | 101 | -0.0728 | 104 |
| | | -0.0855 | 92 | -0.0843 | 102 | -0.0764 | 103 | -0.0817 | 100 | -0.0750 | 102 |
| 8—a b c | 10×10^5 | -0.1073 | 74 | -0.1140 | 77 | -0.1119 | 72 | -0.1076 | 76 | -0.1051 | 74 |
| | | -0.1014 | 77 | -0.1031 | 70 | -0.1007 | 71 | -0.0954 | 76 | -0.0966 | 71 |
| | | -0.1058 | 72 | -0.1020 | 72 | -0.1013 | 74 | -0.0949 | 76 | -0.1001 | 71 |
| 9—a b c | 15×10^5 | -0.1207 | 58 | -0.1181 | 66 | -0.1218 | 61 | -0.1238 | 65 | -0.1165 | 59 |
| | | -0.1129 | 60 | -0.1120 | 64 | -0.1113 | 64 | -0.1109 | 67 | -0.1075 | 61 |
| | | -0.1149 | 61 | -0.1107 | 67 | -0.1054 | 66 | -0.1036 | 67 | -0.1028 | 68 |

^a The loss in weight is for a pack of six 1 by 6 in. strips, whereas the tensile strength determinations represent the average of six values. All samples had ten passes under the beam at the indicated dosage, with 1 hr postheating at 75 C after each pass. The general averages for conditions "a," "b," and "c" for the five atmospheres give values of 136.6, 135.6, and 134.2 respectively. The loss in tensile strength for the general average, accordingly, from the conditions of "a" to those of "c" is 1.75 per cent. The general averages for conditions "a," "b," and "c" for loss of weight in all atmospheres give values of -0.0753, -0.0674 and -0.0655, or a 13.7 per cent change from "a" to "c." There is indication, accordingly, of deterioration from "a" through "b" to "c" treatments.

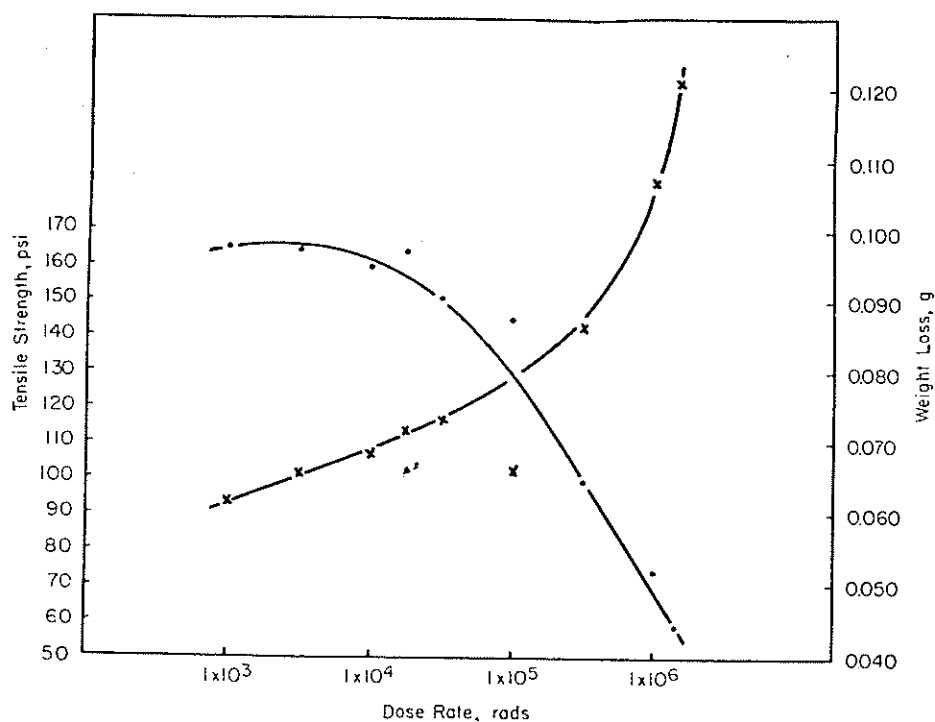


FIG. 5.—Cotton Duck (Sample D-637 a): Postirradiation Effects in Air. Tensile strength indicated by dots; weight loss indicated by crosses.

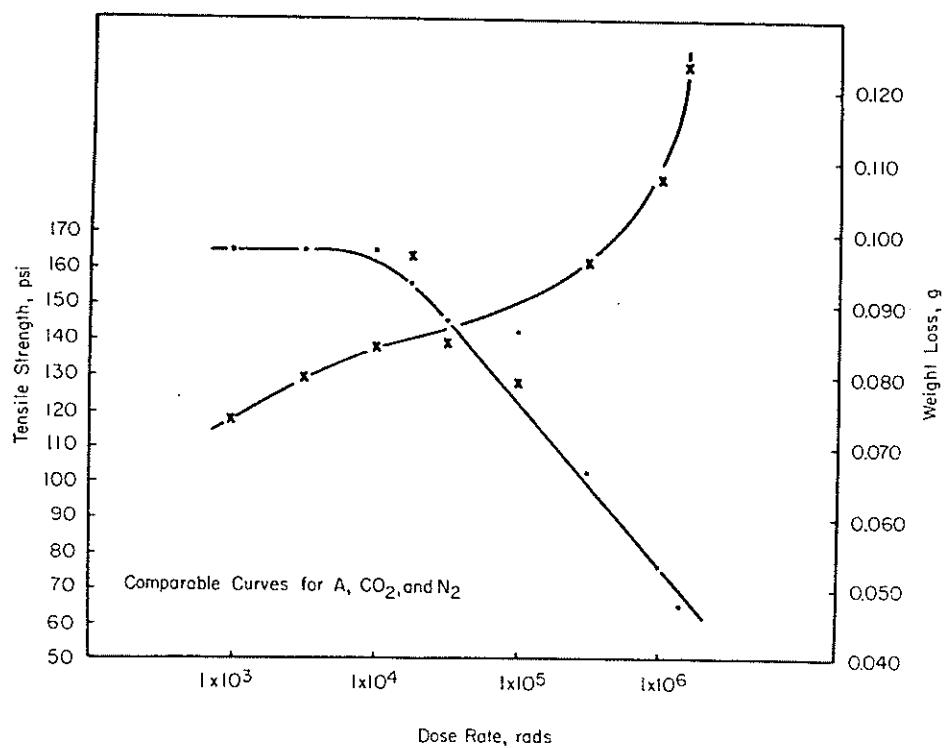


FIG. 6.—Cotton Duck (Sample D-640 a): Postirradiation Effects in Helium. Tensile strength indicated by dots; weight loss indicated by crosses.

to study the effect of dose rate, atmosphere, and postirradiation storage conditions.

The cotton duck was cut into 1 by 6 in. strips with the length in the warp direction, assembled in packets of six each, oven heated for 2 hr at 100 C, conditioned in the balance room for three days, and the packets carefully weighed to determine the initial weight. Each packet was then transferred to a 1 by 12 in. pyrex test tube and the tubes constricted near the neck so as to permit

weight. Tensile strength determinations were then made; the average of the six readings for each packet is shown in Table IV. Graphic representations of the data obtained for atmospheres of air and helium are given by Figs. 5 and 6.

The averages of the "a," "b," and "c" samples for the five atmospheres give tensile strengths of 136.6, 135.6, and 134.2 lb per in. respectively, which represents a decrease of 1.75 per cent from "a" conditions through "b" conditions to "c" conditions, which suggests that postheat-

TABLE V.—COTTON DUCK: POSTIRRADIATION EFFECTS^a AT DIFFERENT DOSE RATES, ATMOSPHERES, AND POSTIRRADIATION STORAGE CONDITIONS.

| Atmosphere | Condition a, Processed, Tensile Strength, avg, lb per in. | Condition b, 47½ days at 0 C, Tensile Strength, avg, lb per in. | Condition c, 47½ days at 50 C, Tensile Strength, avg, lb per in. |
|-------------------------------------|---|--|---|
| Air (D-637) | 137 | 136 | 128 |
| Argon (D-638) | 139 | 137 | 136 |
| Carbon dioxide (D-639) | 134 | 134 | 135 |
| Helium (D-640) | 136 | 134 | 134 |
| Nitrogen (D-641) | 137 | 135 | 136 |

^a General average from 66 samples: controls, heat controls, and nine dose rates.

sealing in the desired atmosphere. The constricted tubes were then placed on a manifold, evacuated, flamed out, and the desired atmosphere introduced. With two additional evacuations and fillings of the indicated atmosphere, they were sealed off and strip packaged in polyethylene for irradiation. The "a" samples (Table IV) were processed promptly; the "b" samples were refrigerated for 47½ days; and the "c" samples were heated at 50 C for 47½ days.

The packets were then removed from the test tubes and placed in the conditioned balance room for three days and weighed to determine any change in

TABLE VI.—COTTON DUCK: POSTIRRADIATION EFFECTS^a AT DIFFERENT DOSE RATES, ATMOSPHERES, AND POSTIRRADIATION STORAGE CONDITIONS.

| Atmosphere | Condition a, Processed, Weight Loss, g | Condition b, 47½ days at 0 C, Weight Loss, g | Condition c, 47½ days at 50 C, Weight Loss, g |
|-------------------------------------|--|---|--|
| Air (D-637) | -0.0761 | -0.0680 | -0.0695 |
| Argon (D-638) | -0.0663 | -0.0628 | -0.0618 |
| Carbon dioxide (D-639) | -0.0763 | -0.0673 | -0.0659 |
| Helium (D-640) | -0.0873 | -0.0752 | -0.0722 |
| Nitrogen (D-641) | -0.0719 | -0.0630 | -0.0581 |

^a General average loss from 66 samples: controls, heat controls, and nine dose rates.

ing might cause additional deterioration. Similarly, the averages of the "a," "b," and "c" samples for loss of weight in all atmospheres are -0.0753, -0.0674, and -0.0655 respectively, or a change from "a" conditions to "c" conditions of 13.7 per cent. The relatively consistent decrease in weight loss from "a" to "c" conditions might result, as a consequence of postheating, from increased oxidation and the production of cleavage products with a higher capacity for moisture retention. The "c" values for weight loss in air and in nitrogen (Table VI) are -0.0695 and -0.0581 respectively, which suggests that the increase in moisture-retention capacity might be more

important than the uptake of oxygen, inasmuch as relatively little (0.3 per cent) oxygen was present in the nitrogen atmosphere. The average weight loss of the group 0-c samples for the five atmos-

tions "a," "b," and "c," irrespective of dose, for tensile strengths of cotton duck irradiated in air are 137, 136, and 128 (Table V). The lowest average value appearing elsewhere in Table V is 134. It

TABLE VII.—COTTON DUCK: POSTIRRADIATION EFFECTS AT DIFFERENT DOSE RATES, ATMOSPHERES, AND POSTIRRADIATION CONDITIONS IN WEIGHT LOSS.

(Compiled from Table IV)

| Dose Rate, rads | Differences in Conditions | Differences in Values in | | | | |
|------------------------|---------------------------|--------------------------|-------|----------------|--------|----------|
| | | Air | Argon | Carbon Dioxide | Helium | Nitrogen |
| Control..... | a - b | 3 | 603? | 75 | 113 | 173 |
| | a - c | 19 | 620? | 113 | 134 | 329 |
| Heat Control..... | a - b | 113 | 41 | 98 | 76 | 52 |
| | a - c | 109 | 13 | 110 | 137 | 80 |
| 1×10^3 | a - b | 84 | 235 | 104 | 91 | 120 |
| | a - c | 57 | 312 | 98 | 68 | 141 |
| 5×10^3 | a - b | 87 | +227 | 86 | 79 | 89 |
| | a - c | 81 | +137 | 90 | 101 | 104 |
| 10×10^3 | a - b | 77 | +123 | 175 | 92 | +3 |
| | a - c | 46 | +112 | 86 | 127 | +7 |
| 25×10^3 | a - b | 81 | 75 | 48 | 233 | 71 |
| | a - c | 41 | 54 | 88 | 240 | 300 |
| 50×10^3 | a - b | 102 | 65 | 91 | 150 | 106 |
| | a - c | 184 | 128 | 157 | 236 | 203 |
| 10×10^4 | a - b | 85 | 688 | +5 | 123 | 106 |
| | a - c | 45 | 621 | 9 | 154 | 114 |
| 50×10^4 | a - b | 69 | 64 | 121 | 126 | 94 |
| | a - c | 10 | 44 | 134 | 138 | 72 |
| 10×10^5 | a - b | 59 | 109 | 112 | 122 | 85 |
| | a - c | 15 | 120 | 106 | 127 | 50 |
| 15×10^5 | a - b | 78 | 61 | 105 | 129 | 90 |
| | a - c | 58 | 74 | 164 | 202 | 137 |

pheres is -0.0519 whereas the corresponding value for the group 9-c samples is -0.1075 or a change of over 107 per cent (see Figs. 5 and 6). The average tensile strengths for "a," "b," and "c" conditions by atmosphere, irrespective of dose rate, are given in Table V, and the comparable weight losses are recorded in Table VI. The average values for condi-

seems likely, therefore, that the 128 value is significantly low and that the post-heating of irradiated cotton in air does increase the deterioration.

For a further evaluation of the data in Table IV, one may tabulate the results obtained from the values of conditions "a" minus "b" and those of conditions "a" minus "c" by dose rate and atmos-

phere as shown in Table VII. It is observed also that out of 110 cases, the values of "a" are larger than those of either "b" or "c" except in seven cases which are indicated by a plus sign. It is noted, moreover, that the values of "a" minus "b" and those of "a" minus "c" for a given set of conditions are usually in better agreement than are the values of Table VII as one goes from dose rate to dose rate or from atmosphere to atmosphere. Inasmuch as the error due to weighing for the results in Table VII is of the order of ± 2 mg, the wide deviations in this table must be considered to be significant pending further study as to their implications.

Closely related work is that of Glegg and Kertesz on the aftereffect in the degradation of cellulose and pectin when exposed to gamma rays, in which they observed a change in viscosity immediately following irradiation and a subsequent change upon storage.⁶

⁶ R. E. Glegg and Z. I. Kertesz, "After-Effects in the Degradation of Cellulose and Pectin by Gamma-Rays," *Science*, Vol. 124, p. 893 (1956).

SUMMARY

The data presented support the postulate that changes or reactions initiated during an irradiation exposure may continue to be operative upon the removal of the irradiation source and might be accelerated by a postheating period.

A postirradiation effect on polymerization has been demonstrated for styrene in five atmospheres, but it is more pronounced in air than it is in argon, carbon dioxide, helium, or nitrogen. The postirradiation effects increase as the total dose increases.

Cotton duck presents a more complex system, but the average tensile strength in air appears to be significantly lower than that obtained in the other atmospheres. The tensile strength decreases and the loss in weight increases as the dose rate increases, but the "c" samples (postheated at 50 C) evidenced a smaller loss in weight than did the "a" samples (processed promptly) and the "b" samples (refrigerated). This is attributed to an oxygen uptake and to the formation of cleavage products which have a greater capacity for moisture retention.